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(54) Title of the Invention: **Porous Polyolefin Hollow Fiber**

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SPECIFICATION

1. Title of the Invention

Porous Polyolefin Hollow Fiber

2. Claims

1. A porous hollow fiber consisting of a polymer blend that comprises 95 to 40 wt% polyolefin and 5 to 60 wt% hydrophilic polyolefin, wherein said porous polyolefin hollow fiber is characterized by having a porous structure in which spaces that are surrounded by lamellae and by the numerous fibrils that connect these lamellae with each other extend throughout the circumferential wall portions of said hollow fiber from the outer wall surfaces to the inner wall surfaces.

2. A porous hollow polyolefin fiber as defined in claim 1, characterized by the fact that the contact angle of the hydrophilic polyolefin with water is 80° or lower, as measured when said polyolefin is in a film state.

3. Detailed Description of the Invention

Field of Industrial Utilization

The present invention relates to a hydrophilic porous hollow fiber suitable for performing filtration, separation, and other operations in medical and industrial applications.

Prior Art

Separation by macromolecular membranes has been widely used for some time, and various materials have been developed for such macromolecular membranes.

Of these, particularly noteworthy are products obtained by melt-spinning crystalline thermoplastic macromolecules into hollow fibers, drawing the fibers at a comparatively low temperature to form crazes in the amorphous regions between the crystal lamellae, and preferably hot-drawing the product to form porous structures in the circumferential wall portions of the hollow fibers. Because no additives or solvents are used to form micropores, these products are used as hollow-fiber

membranes suitable for use in applications in which the elution of impurities or compounds into the system is unacceptable.

The manufacture of such hollow fibers is described in Japanese Laid-Open Patent Applications 52-137026, 57-42919, 57-66114, and elsewhere. The porous hollow fibers manufactured by this method consist of polyolefins or fluoropolyolefins alone, and the material is essentially hydrophobic, with the result that very high pressures are needed to filter aqueous solutions and other aqueous liquids if the fibers are used directly. Such high pressures are impractical, however. In view of this, the fibers are treated with alcohols, surfactants, and other hydrophilizing agents when used to filter aqueous liquids.

Japanese Laid-Open Patent Application 55-137208 describes a method in which two different types of polymers are blended together; the blend is melt-spun and drawn to cleave the interfaces between the polymers of different types, yielding microporous hollow fibers that have nonuniform micropore wall surfaces in which at least some portions of the continuous micropore wall surfaces leading from the outer wall surfaces to the inner wall surfaces of the hollow fiber circumferential walls are composed of a polymer whose properties differ from those of the other polymer; and the side-chain groups present in the constituent polymers are subjected to hydrolysis, sulfonation, or other aftertreatment to manufacture hydrophilic porous hollow fibers in which the surfaces of the micropores have been rendered hydrophilic.

Problems Which the Invention Is Intended to Solve

Medical applications of porous membranes include plasma skimming, filtration of infusion solutions, separation of plasma protein, and manufacture of sterile solutions, whereas industrial applications include washing of integrated circuits, manufacture of water for food processing, and purification of other types of process water. Porous membranes are now extensively used in water purifiers employed in households, eating and drinking establishments, and the like. All these applications involve drainage processes. The elution of foreign matter from porous membrane materials is undesirable because it lowers safety and results in lower-quality purified water or aqueous solutions, so a need existed for membranes in which such elution would not be a concern.

On the other hand, hollow fibers that are rendered porous by melt-spinning polyolefin polymers and drawing the spun product are advantageous in that elution is unlikely to occur during membrane use because no extraction additives or solvents are used. Disadvantages of such fibers, however, are that a hydrophilization treatment is necessary, that the treatment with alcohols or surfactants represents a temporary hydrophilization, and that the alcohols or surfactants migrate into purified water and contaminate it when the hydrophilized fibers are directly used to perform filtration or the like, with the result that these hydrophilizing agents must be thoroughly washed out and removed prior to filtration, and the membrane surface again becomes hydrophobic when dried in such a state, so that replacement with water is needed following hydrophilization, and constant contact with water must be provided.

The approach adopted for the fibers that are rendered porous by melt-spinning and drawing blends of different types of polymers in accordance with the method described in Japanese Laid-Open Patent Application 55-137208 is to cleave the interfaces between different types of polymers rather than to form crazes in the noncrystalline portions between lamellae, making them into fibrils. The resulting disadvantage, therefore, is that in comparison with a case in which crazes are formed in the noncrystalline portions between the lamellae, and the material is made into fibrils, the area of the pore inner surfaces is reduced, the pore diameter is affected by the manner in which the different types of polymers are blended, and pores are formed using the lack of affinity between the different types of polymers, making intimate blending comparatively difficult to achieve and increasing the nonuniformity of pore diameters. Another disadvantage is process complexity brought about by the need for the hydrolysis, sulfonation, or other type of aftertreatment aimed at rendering the product hydrophilic.

Means Used to Solve the Above-Mentioned Problems

As a result of painstaking research conducted in view of this situation, the inventors arrived at the present invention as a result of painstaking research [sic] aimed at developing a technology which could be used to manufacture in a commercially advantageous manner a porous hollow fiber that has permanent hydrophilic properties suitable for treating aqueous liquids and that retains the excellent characteristics of porous hollow fibers obtained by melt-spinning and drawing a polyolefin to form crazes in the noncrystalline portions between the lamellae and to render the material porous.

Specifically, the essence of the present invention resides in a porous hollow fiber consisting of a polymer blend that comprises 95 to 40 wt% polyolefin and 5 to 60 wt% hydrophilic polyolefin, wherein said porous polyolefin hollow fiber is characterized by having a porous structure in which spaces that are surrounded by lamellae and by the numerous fibrils that connect these lamellae with each other extend throughout the circumferential wall portions of said hollow fiber from the outer wall surfaces to the inner wall surfaces.

Examples of the polyolefins that can be used in the present invention include polyethylene, polypropylene, poly(3-methylbutene-1), and poly(4-methylpentene-1). The hydrophilic polyolefin that is blended with the polyolefin in accordance with the present invention should be a polyolefin modified in such a way that when it is made into a film and measured, its contact angle with water is 80° or less. It is even better to use a polyolefin modified in such a way that the contact angle is 70° or less. Examples of polymers modified in such a manner include various polyolefins in which hydroxyl groups, carboxyl groups, amino groups, sulfonic acid groups, polyoxyethylene groups, and other groups are bonded to the molecular chains. Other examples include copolymers of ethylene and vinyl alcohol, copolymers of ethylene and vinyl acetate, copolymers of ethylene and maleic anhydride, copolymers in which ethylene and polyoxyethylene are chemically bonded, and polyolefins cross-linked by metal ions.

The reason that the polymers blendable with polyolefins in this case are limited to hydrophilic polyolefins is that when a hydrophilic polyolefin is blended with another polyolefin, satisfactory affinity between the two polyolefins results, so there is no substantial impediment to the formation of a highly oriented, highly crystalline lamellar structure along the circumferential walls of the undrawn hollow fibers obtained by the melt drawing of the blend, and it is less likely that separation will occur along the interface of the components of the polymer blend. This yields the same excellent porous membrane structure as when a polyolefin polymer alone is used. Another advantage is that because the material contains hydrophilic groups, permanent hydrophilic properties are afforded, water and moisture can penetrate freely, and the spaces around fibrils consist of air pores. This substantially reduces clogging because detours readily form when one of the air pores is blocked. The compounding ratio of the polyolefin and hydrophilic polyolefin should be 95 to 40 wt% polyolefin and 5 to 60 wt% hydrophilic polyolefin. This is because when a highly hydrophilic material is

used as the hydrophilic polyolefin, hydrophilic properties can be obtained with a comparatively small amount of the blend, whereas when a large amount of such a hydrophilic polyolefin is blended, the formation of lamellar crystals tends to be impeded, making it difficult to obtain a satisfactory porous structure and resulting in comparatively poor hydrophilic properties of the material. By contrast, a material that has more polyolefin features must be blended in a comparatively large amount to obtain satisfactory hydrophilic properties, but the formation of lamellar crystals is not impeded when a large amount of the material is blended. The compounding ratio of the polyolefin and hydrophilic polyolefin should be 90 to 50 wt% polyolefin and 10 to 50 wt% hydrophilic polyolefin. It is unsuitable for the polyolefin ratio to be lower than the aforementioned lower limit or higher than the aforementioned upper limit, because in the first case it becomes more difficult to obtain a sufficiently uniform porous structure, and in the second case the hydrophilic properties become inadequate.

Because the porous hollow fiber of the present invention has a structure that is obtained by drawing undrawn hollow yarns (fabricated by spinning crystalline macromolecules) and stretching the molecules folded between the lamellae of the undrawn yarns to cleave said molecules into fibrils, spaces form around the numerous fibrils that are oriented along the fibers and that connect the lamellae with each other, and this structure stretches from the outer wall surface to the inner wall surface of the peripheral wall portion of the hollow fiber.

A method for manufacturing the porous fiber of the present invention will now be described.

The aforementioned polyolefin and hydrophilic polyolefin are first blended, and the blending operation must yield a sufficiently uniform blend. The aforementioned polymers should therefore be blended in advance using, for example, a blender such as a V-type blender, or blended in the molten state in a melt extruder and then pelletized, and the pellets introduced into an extruder for melt spinning.

The resulting polymer blend is subsequently spun in the molten state using a nozzle for hollow fibers. Because of minimal thickness nonuniformity, nozzles with double-pipe structures should be used as the nozzles for hollow fibers. It is apparent that horseshoe-shape nozzles or the like can be used as long as they are nozzles for hollow fibers.

The spinning temperature of melt spinning should be suitably set in conjunction with the type of polymer used, the melt index, the discharge rate adopted, the cooling conditions, the winding speed, and other conditions, but should still remain within a range which can stably ensure the desired thickness and inside diameter of the hollow fiber. Under ordinary conditions, spinning should be performed at a temperature which is at least 20°C higher than the melting point (hereinafter " m_{pH} ") of the highest-melting polymer (of the polymers comprising the blend) but no more than 100°C higher than said melting point (m_{pH}). It is unsuitable to perform spinning at a temperature lower than the lower limit of this temperature range, because although the resulting undrawn yarns are highly oriented, the maximum draw ratio attainable during the subsequent drawing process for fabricating a drawn porous material is lowered, and a sufficiently high porosity is difficult to obtain. Nor is it desirable to perform spinning at a temperature that exceeds the upper limit of the aforementioned temperature range, because high porosity is difficult to obtain in this case as well.

To endow the undrawn yarns obtained by melt spinning with high orientation and crystallinity, it is better to ensure a spinning draft of 100 to 10,000, and preferably 1000 to 10,000. When the spinning draft is lower than 100, the lamellar crystal structure is formed unsatisfactorily, making it difficult to form a satisfactory porous structure even after the subsequent drawing process. The undrawn filaments obtained by melt spinning should have a "hollow" inside diameter of 50 to 2000 μm and a film thickness of 10 to 200 μm . Dimensions that fall outside these ranges may also be used when necessary, however.

The undrawn hollow fiber thus obtained can be drawn without undergoing any additional treatments, or, to improve orientation and crystallization, it can be drawn after being annealed under constant-length or relaxation conditions at a temperature which does not exceed m_{pH} and falls within a temperature range within which the structure of the undrawn yarns is hardly damaged at all.

The porous hollow fiber of the present invention is obtained by drawing the resulting undrawn yarns and rendering them porous. Drawing should be a combination of cold drawing (at temperature ranging from $m_{pH} - 80^\circ\text{C}$ or lower to $m_{pH} - 220^\circ\text{C}$ or higher, and preferably $m_{pH} - 160^\circ\text{C}$ to $m_{pH} - 90^\circ\text{C}$) and subsequent hot drawing (at a temperature ranging from $m_{pH} - 60^\circ\text{C}$ to $m_{pH} - 5^\circ\text{C}$). The hot drawing may be a multistep drawing operation consisting of two or more steps. The desired porous structure cannot be obtained when the hot drawing temperature is higher than the

aforementioned upper limit. It is unsuitable for the hot drawing temperature to be lower than the aforementioned lower limit because porosity decreases with a reduction in temperature.

The draw ratio of cold and hot drawing should be suitably set in accordance with the porosity of the porous hollow fiber and other desired quality characteristics, but the draw ratio of cold drawing should be 10 to 100%, and the draw ratio of hot drawing should be set in such a way that the combined draw amount of cold drawing and hot drawing is 150 to 900%. A total draw amount that exceeds 700% is unsuitable because of frequent yarn breakage during drawing. Hot drawing endows the porous polyolefin fiber thus obtained with substantial shape stability, although heat setting may also be performed as needed at a temperature ranging from $m_{pH} - 60^{\circ}\text{C}$ to $m_{pH} - 5^{\circ}\text{C}$ under conditions of stretching or limited relaxation. The inventors learned that the properly set temperature, draw ratio, and other parameters of cold and hot drawing can yield the desired porosity, blockage ratio (during filtration), and other quality characteristics of porous hollow fibers.

Practical Examples

The present invention will now be described in further detail through practical examples. In these practical examples, the crystallinity of polymer blends was determined by integrating the refraction intensity in all directions using a wide-angle x-ray diffraction apparatus, and calculating the crystallinity using the following formula.

$$\text{Crystallinity } \chi_c = (\text{Integral of total diffraction intensity} - \text{Integral of diffraction intensity of noncrystalline portion}) / \text{Integral of total diffraction intensity}$$

In addition, the degree of crystalline orientation was determined by first calculating the half value of the distribution of the diffraction intensity of the (110) plane along different fiber axes using a wide-angle x-ray diffraction apparatus, and then calculating the degree of crystalline orientation using the following formula.

$$\text{Degree of crystalline orientation} = (H_{(110)} / (180 - H_{(110)})) \times 100 (\%)$$

In the formula, $H_{(110)}$ is the half value of the (110) plane.

The contact angle with water in a film state was measured by a known method using a Kyowa Contact Angle Meter manufactured by Kyowa Kagaku.

Practical Example 1

A high-density polyethylene ("Hi-Zex 2200J," manufactured by Mitsui Petrochemical) with a density of 0.968 g/cm^3 and a product ("Hi-Miran-1702"; manufactured by Mitsui Polychemical; contact angle with water in a film state: 69°) obtained by cross-linking a copolymer of polyethylene and acrylic acid with zinc ions were dried after being blended in a 1:1 ratio in a V-type blender. Air was fed in a self-contained mode using a nozzle which was designed for the manufacture of hollow fibers and which had a double-pipe structure with a discharge port diameter of 28 mm and a circular pipe slit width of 3.5 mm. The blend was wound after being spun at a spinning temperature of 170°C , a spinning draft of 3400, and a spinning rate of 200 m/min.

The resulting undrawn yarns were heat-treated for 120 seconds at 115°C under conditions of constant length. The undrawn yarns had a crystallinity of 62% and a degree of crystalline orientation of 75%. These undrawn yarns were first cold-drawn to 80% at 25°C and then hot-drawn in a heating box (heated to 115°C) with a length of 2 m until the total draw ratio reached 520%. Relaxation and heat setting were then performed in a heating box (with a length of 2 m heated to the same temperature) in such a way that the total draw ratio was 400%.

The resulting porous hollow fiber had an inside diameter of $270 \mu\text{m}$, a film thickness of $51 \mu\text{m}$, a porosity of 62%, and a water penetration pressure (hydraulic pressure at which water penetrated uniformly through the surface of the hollow fiber) of 1.1 kg/cm^2 .

Practical Example 2

A high-density polyethylene with a density of 0.968 g/cm^3 and a product obtained by cross-linking a copolymer of polyethylene and acrylic acid with zinc ions were blended in a 1:1 ratio in a V-type blender. The same operations as those employed in Practical Example 1 were then performed, except that the dried product was replaced with a product obtained by blending a high-density polyethylene ("Hi-Zex 2200J," manufactured by Mitsui Petrochemical) having a density of 0.968 g/cm^3 with an ethylene-vinyl alcohol copolymer ("Soanol D"; manufactured by Nippon Synthetic

Chemical; contact angle with water in a film: 56°) in a 7:3 ratio in an extruder, and drying the blend. The heat-treated, undrawn hollow fiber had a crystallinity of 68% and a degree of crystalline orientation of 82%.

The porous hollow fiber obtained by drawing and heat setting had an inside diameter of $280\text{ }\mu\text{m}$, a film thickness of $55\text{ }\mu\text{m}$, a porosity of 65%, and a water penetration pressure of 1.5 kg/cm^2 .

Comparative Example 1

A high-density polyethylene with a density of 0.968 g/cm^3 and a product obtained by cross-linking a copolymer of polyethylene and acrylic acid with zinc ions were blended in a 1:1 ratio in a V-type blender. The same operations as those employed in Practical Example 1 were then performed, except that the dried product was replaced with a high-density polyethylene ("Hi-Zex 2200J," manufactured by Mitsui Petrochemical) having a density of 0.968 g/cm^3 , yielding a porous hollow fiber. The resulting porous hollow fiber had an inside diameter of $285\text{ }\mu\text{m}$, a film thickness of $58\text{ }\mu\text{m}$, a porosity of 72%, and a water penetration pressure of 4.9 kg/cm^2 .

Merits of the Invention

The hollow fiber of the present invention can be obtained without the use of solvents or extraction additives during manufacture, yielding hollow-yarn membranes with excellent reliability in terms of health and safety. In addition, strength characteristics are improved over the strength characteristics of membranes obtained by conventional wet techniques or extraction techniques. Another advantage is that clogging is minimized because of the formation of the porous structures in which spaces that are surrounded by lamellae and by the numerous fibrils that connect these lamellae with each other extend throughout the circumferential wall portions of said hollow fiber from the outer wall surfaces to the inner wall surfaces. Yet another advantage is that permanent hydrophilic properties are afforded by the use of a blend obtained by blending a hydrophilic polyolefin with a polyolefin serving as the base, yielding excellent characteristics suitable for treating aqueous liquids in medical applications, food industry applications, and the like.